

Competition between crystalline electric field singlet and itinerant states of f electrons

Shinji Watanabe* and Yoshio Kuramoto
Department of Physics, Tohoku University, Sendai 980

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Abstract

A new kind of phase transition is proposed for lattice fermion systems with simplified f^2 configurations at each site. The free energy of the model is computed in the mean-field approximation for both the itinerant state with the Kondo screening, and a localized state with the crystalline electric field (CEF) singlet at each site. The presence of a first-order phase transition is demonstrated in which the itinerant state changes into the localized state toward lower temperatures. In the half-filled case, the insulating state at high temperatures changes into a metallic state, in marked contrast with the Mott transition in the Hubbard model. For comparison, corresponding states are discussed for the two-impurity Kondo system with f^1 configuration at each site.

1 Introduction

In some uranium compounds with $5f^2$ configuration (U^{4+}) the CEF ground-state can be a nonmagnetic singlet. The CEF singlet is also realized in some praseodymium compounds with $4f^2$ configuration (Pr^{3+}). In these cases the spin entropy of the system can go to zero as temperature decreases even though interactions with conduction electrons or with f electrons at other sites are absent. This is in striking contrast with the case of cerium compounds with $4f^1$ configuration (Ce^{3+}); the entropy does not disappear at zero temperature if a Ce ion is isolated because of the Kramers degeneracy associated with the f^1 configuration. As a result the system chooses, depending on the interaction between Ce sites, among a magnetically ordered state, a Fermi liquid state, a superconducting state, and so on in which the entropy vanishes at zero temperature.

In these lattice fermion systems, which we call the f^2 lattice hereafter, the itinerant state is also possible if the hybridization is large enough. Thus both the localized f -electron picture and the band picture can be a starting point to understand the actual compounds with f^2 configuration. The most interesting situation occurs when the energy scale of the CEF singlet state is comparable to that of the itinerant state. Then both states compete for the stability.

Suppose we have the CEF singlet as the ground state of the f^2 lattice, but its energy is only a little lower than the itinerant state. If the itinerant state is metallic, the entropy increases linearly as temperature increases. The temperature scale here is the Kondo temperature, and is related to the large density of states at the Fermi surface. On the other hand increase of the f -electron part of the entropy in the CEF state follows the exponential law, and is much less significant in a low temperature range. Thus there is a possibility for a phase transition to occur from the CEF singlet state to the itinerant state as temperature increases in the f^2 lattice system. Even if the itinerant state is a Kondo insulator, the entropy can increase more rapidly than that in the CEF state since the energy gap decreases with temperature. In the latter case the system changes from a metal to an insulator as temperature increases. This is opposite to the case of the Mott transition where the low-temperature phase is an insulator.

The purpose of this paper is to demonstrate the presence of a phase transition between the CEF singlet and itinerant states in the f^2 lattice system at zero and finite temperatures. As the first step to explore

*e-mail: watanabe@cmpt01.phys.tohoku.ac.jp

an f^2 lattice system, we take the simplest possible approach and apply the mean field approximation with account of both itinerant and localized characters of f electrons. The plan of the paper is as follows: In the next section, we introduce the model and derive the mean-field equations. The same approximation scheme is applied to the two-impurity Kondo system with f^1 configuration at each site in Section 3. It turns out helpful to compare the electronic states of both models. The relative stability of different phases in both the f^2 lattice system and the two-impurity Kondo system is studied in Section 4. Presence of the phase transition at finite temperatures is demonstrated. The final section is devoted to discussion of results with attention to possible experimental relevance.

2 Model and Mean-Field Equations

We introduce an f^2 lattice model as follows:

$$\begin{aligned}
H = & \sum_{\mathbf{k}\sigma} \sum_{\nu=\alpha,\beta} \varepsilon_{\mathbf{k}\nu} c_{\mathbf{k}\nu\sigma}^\dagger c_{\mathbf{k}\nu\sigma} \\
& + J \sum_i \sum_{\nu=\alpha,\beta} \sum_{\mu=1,2} \left(\mathbf{S}_{i\mu}^f \cdot \mathbf{S}_{i\nu}^c + \frac{1}{4} n_{i\mu}^f n_{i\nu}^c \right) \\
& + I \sum_i \left(\mathbf{S}_{i1}^f \cdot \mathbf{S}_{i2}^f + \frac{1}{4} n_{i1}^f n_{i2}^f \right), \tag{1}
\end{aligned}$$

where i is the site index, and ν and μ are channels of conduction and f electrons, respectively. We express the CEF singlet and triplet using a pseudo-spin operator of f electrons for each channel: $\mathbf{S}_{i\mu}^f = (1/2) \sum_{\gamma\delta} f_{i\mu\gamma}^\dagger \vec{\sigma}_{\gamma\delta} f_{i\mu\delta}$, where $\vec{\sigma}$ is the vector composed of Pauli matrices. The spin operator of conduction electrons is given by $\mathbf{S}_{i\nu}^c = (1/2) \sum_{\gamma\delta} c_{i\nu\gamma}^\dagger \vec{\sigma}_{\gamma\delta} c_{i\nu\delta}$. In eq. (1), the second term with $J > 0$ gives antiferromagnetic interaction between f and conduction electrons on each site. In the presence of the potential scattering term $(1/4) n_{i\mu}^f n_{i\nu}^c$, the Kondo scale $T_K = D \exp(-1/J\rho_{c0})$ is reproduced correctly in the mean-field approximation. Here, D is a half width of a conduction band and ρ_{c0} is the density of states per spin of conduction electrons at the Fermi level. We note that the sum of the spin exchange and potential scattering terms is half of the permutation operator whose eigenvalue is 1 for the quasi-spin triplet and is -1 for the singlet. The last term with $I > 0$ in eq. (1) represents the CEF splitting. This splitting I is also correctly given by the mean-field approximation due to the term $(1/4) n_{i1}^f n_{i2}^f$. The restriction $n_{i\mu}^f = 1$ is imposed on eq. (1) to simulate the strong Coulomb repulsion between f electrons.

We take a mean field as

$$V_{i\mu\nu} = -\frac{J}{2} \sum_{\sigma} \langle f_{i\mu\sigma}^\dagger c_{i\nu\sigma} \rangle \tag{2}$$

for $\mu = 1, 2$ and $\nu = \alpha, \beta$. This mean field represents the fictitious hybridization between f and conduction electrons. We say "fictitious hybridization" in the sense that the real hybridization is absent in the model with fixed occupation of f states. However we neglect in this paper the phase fluctuation which makes the mean field vanish. The physical motivation for the neglect will be discussed in the final section. Another mean-field is given by

$$R_i = \frac{I}{2} \sum_{\sigma} \langle f_{i1\sigma}^\dagger f_{i2\sigma} \rangle \tag{3}$$

which expresses the mixing between two f orbitals on each site. This mixing gives rise to bonding-antibonding splitting of localized levels. In eqs. (2) and (3) we assume that the mixing is allowed only for the same spin directions. The Lagrange multiplier terms

$$- \sum_i \sum_{\mu=1,2} \lambda_{i\mu} (n_{i\mu}^f - 1)$$

are added to eq. (1) to enforce the constraints on the number of f electrons. In the mean-field approximation the number of f electron per site and channel is fixed only as average. Therefore care is necessary

about spurious charge fluctuations included. We discuss this aspect of the mean-field theory again in the final section of the paper.

Assuming equivalence of different sites and channels, we put $\varepsilon_{\mathbf{k}\nu} = \varepsilon_{\mathbf{k}}$, $V_{i\mu\nu} = V_{\mu\nu} = |V| \exp(-i\theta_{\mu\nu})$, $R_i = R$ and $\lambda_{i\mu} = \lambda$. Setting the origin of energy at the Fermi level, we write the free energy per site as

$$F = -\frac{T}{N_s} \sum_{\sigma} \sum_{\mathbf{k}, \omega_n} \text{tr} \ln \left[\frac{M(\mathbf{k}, i\omega_n)}{T} \right] + 2 \left(J + \frac{I}{4} - \tilde{\varepsilon}_f \right) + \frac{8\Delta}{J\pi\rho_{c0}} + \frac{2|R|^2}{I}, \quad (4)$$

where N_s is the total number of the sites, $\tilde{\varepsilon}_f = J + I/4 - \lambda$ and $\Delta = \pi\rho_{c0}|V|^2$. The 2×2 matrix M with Matsubara frequency $i\omega_n$ has components

$$M_{\mu\mu} = -i\omega_n + \tilde{\varepsilon}_f + \frac{2|V|^2}{i\omega_n - \varepsilon_{\mathbf{k}}} \quad (\mu = 1, 2), \quad (5)$$

$$M_{12} = -R + \frac{2|V|^2}{i\omega_n - \varepsilon_{\mathbf{k}}} \Xi, \quad (6)$$

$$M_{21} = -R^* + \frac{2|V|^2}{i\omega_n - \varepsilon_{\mathbf{k}}} \Xi^*, \quad (7)$$

where $\Xi = \{\exp(-i\phi_{\alpha}) + \exp(-i\phi_{\beta})\}/2$ with $\phi_{\nu} = \theta_{1\nu} - \theta_{2\nu}$ ($\nu = \alpha, \beta$). Here we represent the magnitude of the hybridization between different channels of f electrons via conduction electrons by the parameter Ξ . Let us take the bases in which the on-site hybridization between f and conduction electrons occurs only with the same channel. Even for this case, the intersite hybridization between the channels 1 and 2 of f electrons can occur. This is because the point group symmetry around each site is not relevant to intersite interactions. From a detailed analysis we find that R and Ξ can be chosen real. Then we can assume $-1 \leq \Xi \leq 1$ in the following.

We derive the mean-field equations by requiring the free energy to be stationary against variation of Δ , $\tilde{\varepsilon}_f$ and R . As a result three characteristic states appear: First the Kondo state is the itinerant state where f-electrons hybridize with conduction electrons ($\Delta \neq 0$, $R = 0$). Secondly the CEF state is the localized state where f-electrons form the singlet of quasi-spins at each site ($\Delta = 0$, $R \neq 0$). Thirdly the mixed state has a character interpolating between the Kondo and CEF states ($\Delta \neq 0$, $R \neq 0$). For the CEF state we always have the solution $\Delta = \tilde{\varepsilon}_f = 0$ and $R = I\{f(-R) - f(R)\}/2$. Here, $f(w) = 1/\{\exp(w/T) + 1\}$ is the Fermi distribution function with energy w .

In the following we consider the case where the number N_c of conduction electrons is twice the number of lattice sites, and the conduction bands without hybridization have constant density of states $\rho_{c0} = 1/(2D)$ between the band edges $\pm D$. Then the system has the insulating ground state if f electrons form energy bands, since f and conduction electrons have the hybridization gap at the Fermi level. This is called the Kondo insulator. If f electrons are localized, on the other hand, the Fermi level lies in the middle of the conduction band, and the system becomes metallic. For the Kondo and mixed states, each conduction band is split into two pieces with a band gap between them. We use the notation $E_{\zeta} = \tilde{\varepsilon}_f - (-1)^{p(\zeta)}R$, and $\Xi_{\zeta} = 1 + (-1)^{p(\zeta)}\Xi$ where $p(a) = 1$, $p(b) = 0$ with $\zeta = a, b$. The band edges after splitting are given by

$$\begin{aligned} D_{1\zeta} &= \frac{-D + E_{\zeta}}{2} - \frac{D + E_{\zeta}}{2} \sqrt{1 + \frac{8\Delta\Xi_{\zeta}}{\pi\rho_{c0}(D + E_{\zeta})^2}}, \\ D_{2\zeta} &= \frac{D + E_{\zeta}}{2} - \frac{D - E_{\zeta}}{2} \sqrt{1 + \frac{8\Delta\Xi_{\zeta}}{\pi\rho_{c0}(D - E_{\zeta})^2}}, \\ D_{3\zeta} &= \frac{-D + E_{\zeta}}{2} + \frac{D + E_{\zeta}}{2} \sqrt{1 + \frac{8\Delta\Xi_{\zeta}}{\pi\rho_{c0}(D + E_{\zeta})^2}}, \\ D_{4\zeta} &= \frac{D + E_{\zeta}}{2} + \frac{D - E_{\zeta}}{2} \sqrt{1 + \frac{8\Delta\Xi_{\zeta}}{\pi\rho_{c0}(D - E_{\zeta})^2}}. \end{aligned}$$

Then the mean-field equations are given by

$$\left(\int_{D_{1b}}^{D_{2b}} + \int_{D_{3b}}^{D_{4b}} \right) dw \frac{4\Delta\Xi_b}{\pi(w - E_b)^2} f(w) = 1 + \frac{2R}{I}, \quad (8)$$

$$\left(\int_{D_{1a}}^{D_{2a}} + \int_{D_{3a}}^{D_{4a}} \right) dw \frac{4\Delta\Xi_a}{\pi(w - E_a)^2} f(w) = 1 - \frac{2R}{I}, \quad (9)$$

$$\begin{aligned} & \left(\int_{D_{1b}}^{D_{2b}} + \int_{D_{3b}}^{D_{4b}} \right) dw \frac{\Xi_b}{w - E_b} f(w) \\ & + \left(\int_{D_{1a}}^{D_{2a}} + \int_{D_{3a}}^{D_{4a}} \right) dw \frac{\Xi_a}{w - E_a} f(w) = -\frac{2}{J\rho_{c0}}. \end{aligned} \quad (10)$$

We solve eqs.(8)-(10) for various values of dimensionless parameters I/T_K and Ξ at zero and finite temperatures. We note that the mixed state is metallic because the condition $R\Delta \neq 0$ requires a finite density of states between bonding and antibonding f levels.

3 Two-Impurity Kondo System

In the course of understanding the electronic state in the f^2 lattice system, a necessary step is to clarify the difference from the f^2 impurity system. This impurity system is further related to the two-impurity Kondo system with f^1 configuration at each site. Namely, the f^2 impurity is considered as the short-distance limit of two Kondo impurities. Fortunately we have detailed knowledge about the two-impurity system by the mean-field theory [1], the Quantum Monte Carlo [2], and the numerical renormalization group [3, 4]. In this paper we derive the ground state and the free energy in the same level of approximation as is used for the f^2 lattice system. Then by comparing the electronic state of the f^2 lattice system and that of the impurity system, we obtain information about the influence of the lattice periodicity.

In ref. [1] the two-impurity Anderson model was solved by the mean-field theory. It was shown that the intersite hybridization gives smooth change from the limit of two independent Kondo states (Kondo pair) to the pair singlet state as the intersite interaction increases. Physically we expect the same situation even though the occupation of f electrons at each site is very close to unity. The limiting case is described by the two-impurity Kondo model. Although the Anderson lattice model is more general than the Kondo lattice model, the CEF state is harder to treat in the mean-field theory. Since we have adopted the Kondo lattice model with f^2 configurations, we need to solve the two-impurity Kondo model for comparison.

The two-impurity model is given by

$$\begin{aligned} H_{2\text{imp}} &= \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + J \sum_{j=1}^2 \left(\mathbf{S}_j^f \cdot \mathbf{S}_j^c + \frac{1}{4} n_j^f n_j^c \right) \\ &+ I \left(\mathbf{S}_1^f \cdot \mathbf{S}_2^f + \frac{1}{4} n_1^f n_2^f \right), \end{aligned} \quad (11)$$

where $J, I > 0$ and $j(=1, 2)$ labels sites of f electrons. There is only a single conduction band since even in this case different screening channels are present around each impurity. We take the mean-fields in the form analogous to the f^2 lattice system: One is given by

$$V_j = -\frac{J}{2} \sum_{\mathbf{k}\sigma} e^{i\mathbf{k} \cdot \mathbf{r}_j} \langle f_{j\sigma}^\dagger c_{\mathbf{k}\sigma} \rangle$$

which represents the fictitious hybridization between f and conduction electrons at each site. The other is given by

$$R = \frac{I}{2} \sum_{\sigma} \langle f_{1\sigma}^\dagger f_{2\sigma} \rangle$$

which expresses the mixing between two f electrons. As before the Lagrange multiplier terms

$$- \sum_{j=1,2} \lambda_j (n_j^f - 1)$$

are added to eq. (11) to enforce the constraints on the number of f electrons.

There are two dimensionless parameters A, B which represent the intersite hybridization effect via conduction electrons. Namely we define

$$|V|^2 \sum_{\mathbf{k}} \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{i\omega_n - \varepsilon_{\mathbf{k}}} = [B + iA \text{sgn}(\omega_n)] \Delta. \quad (12)$$

Here, the magnitudes of A and B depend on both the distance \mathbf{r} between f sites and the band structure of conduction electrons, but they are always less than unity [1]. The parameter A causes asymmetry in the density of states of bonding and antibonding f states: In the case $R > 0$, with $A > 0$ (< 0) the density of states of the bonding states becomes wider (narrower) than that of the antibonding states. On the other hand the parameter B controls the splitting between bonding and antibonding f states. The left-hand side of eq. (12) is analogous to the term with Ξ in eq. (6) if one interchanges sites in the former with channels in the latter. In the two-impurity system there are three characteristic states: The first is the Kondo-pair state where the Kondo effect occurs independently at each site ($\Delta \neq 0, R = 0$); the second is the pair-singlet state where the pair-singlet of f electrons is formed without help of conduction electrons ($\Delta = 0, R \neq 0$); the third is the mixed state which interpolates the above two states ($\Delta \neq 0, R \neq 0$).

4 Stability of Itinerant and Localized States

4.1 Zero temperature

We have solved the mean-field equations numerically at zero temperature both for the f^2 lattice and the two-impurity systems. Table 1 summarizes the parameters used in the calculation. Figure 1(a) shows the ground-state energy per site in the f^2 lattice system at zero temperature. The origin of energy is taken to be that of the Fermi sea without f electrons. The abscissa represents the bare CEF splitting in units of T_K . The notations E_K , E_{CEF} and E_{mix} represent the ground-state energies of Kondo, CEF and mixed states, respectively. The effect of intersite hybridization Ξ depends only on its absolute value. Thus results of E_{mix} with $\Xi = 0$ and $\Xi = 0.4$ are shown as representative cases in Fig. 1(a).

We find that E_{mix} is larger than E_K and E_{CEF} for all combinations of parameters I/T_K and Ξ . Therefore the change from the Kondo state to the CEF state occurs discontinuously at the critical point $I/T_K = 4$. The mixed state which would have interpolated the Kondo and CEF states smoothly is not stabilized actually; with increasing intersite hybridization, the mixed state with energy E_{mix} becomes larger in the mean-field theory. This is seen by the fact that E_{mix} with $\Xi = 0.4$ is larger than that with $\Xi = 0$ in Fig. 1(a). The reason is the following: If $\Xi > 0$ and $R > 0$, the density of states of the bonding f states has a larger width than that of the antibonding f states. The ground-state energy is given by the sum of single-particle energies of occupied states. Namely, we integrate the total density of states multiplied by w from $-\infty$ to 0. Since the integral without w is fixed by the number conservation, the total energy increases by the asymmetry induced by Ξ . Similarly in the case of $\Xi < 0$ and $R > 0$, the asymmetry of the density of states in the opposite direction increases the energy again.

For comparison, Fig.1(b) shows the ground-state energy of f electrons in the two-impurity system at zero temperature. We have tried various values of A and confirmed that A does not influence the relative stability of the phases. On the contrary the value of B drastically affects the ground state. Hence, we fix $A = -0.2$ and vary B as a free parameter. We note that if $B = 0$, E_{mix} is larger than both E_K and E_{ffpair} for any value of I/T_K . This situation is analogous to that in the f^2 lattice system. As a result an abrupt change from the Kondo-pair state to the pair-singlet state occurs as I/T_K is increased. At the critical point of $I/T_K = 2.5$, the two kinds of singlet states are degenerate. Thus one observes the divergence of physical quantities such as the susceptibility and the specific heat coefficient. We have checked that this level-crossing behavior remains the same as long as $|B| < 1/\pi$. On the contrary, if the hybridization effect is large ($1/\pi < |B| < 1$), the Kondo-pair state connects continuously with the pair-singlet state

through the mixed state. In this case no divergence occurs. This is shown in Fig.1(b) by the result that $E_{\text{mix}}(B = 0.4)$ is lower than both E_K and E_{ffpair} for any value of I/T_K . These results obtained in the mean-field approximation agree with those in refs. [2, 4, 1] for the two-impurity Anderson model.

We note that A controls asymmetry of the density of states of f electrons with respect to the Fermi level, just as Ξ does in the f^2 lattice system. We have confirmed that E_{mix} becomes larger as $|A|$ increases with B being fixed. Thus the parameter A plays the same role as Ξ in the f^2 lattice system. However in the lattice system we do not have the parameter corresponding to B in the impurity system. Hence there is no stable mixed state in the f^2 lattice system in our calculation. Mathematically the ineffectiveness Ξ in stabilizing the mixed state comes from the absence of \mathbf{k} -summation in the self-energy of the f^2 lattice system.

4.2 Finite Temperature

The mean-field equations are solved numerically also at finite temperatures, and the free energies are derived. Figure 2(a) shows temperature dependence of free energies per site for three different states in the f^2 lattice system: Kondo, CEF and mixed states. Even though the CEF singlet is the ground state, there is a case where the itinerant state is realized at higher temperatures. We find that the free energy of the mixed state is larger than those of the other two states for all values of parameters I/T_K and Ξ . Therefore, the transition between the Kondo and CEF phases occurs as a first-order one.

Figure 2(b) shows free energies in the two-impurity system. The notations F_K , F_{ffpair} and F_{mix} represent the free energies of the Kondo-pair, pair-singlet and mixed states, respectively. It is seen that with $B = 0$, F_{mix} is larger than F_K and F_{ffpair} . As in the case of zero temperature, the mixed state is not stabilized as long as $|B| < 0.08$ for all values of I/T_K . On the other hand, F_{mix} with $B = 0.4$ in Fig. 2(b) is lower than both F_K and F_{CEF} . We have checked that with $0.08 < |B| < 1$ the mixed state is stabilized at all temperatures.

From these results we infer that the parameter B in the two-impurity system plays a decisive role also at finite temperatures. Furthermore in the f^2 lattice system there is no temperature region where the mixed state is stabilized. In other words, the hybridization effect which mediates between Kondo and CEF phases is ineffective, and the transition occurs discontinuously.

5 Discussions

5.1 Comparison with two-impurity systems

In considering the relevance of the mean-field theory, we first take the case of impurity systems. The physical difference between the two-impurity Kondo and Anderson models is whether there is charge fluctuations of f electrons or not. Reliable knowledge is available for both models from several numerical calculations. Computation using the numerical renormalization group derived a level crossing between the Kondo-pair state and the pair-singlet state [3]. As a result divergence of the staggered susceptibility occurs at zero temperature. On the contrary, a quantum Monte Carlo calculation for the two-impurity Anderson model [2] found continuous behavior in physical quantities. This apparent conflict was resolved by Sakai et al. [4] who identified the origin of the continuous crossover as the bonding-antibonding splitting of f orbitals. In the Kondo model, the splitting is absent because there is no charge degrees of freedom for f electrons. Thus the divergent behavior is purely a formal consequence of the model since there should always be some amount of charge fluctuations in real systems.

For our purpose of studying a new type of phase transition, we regard our model given by eq.(1) only as a simplified form of Anderson-type models which are more difficult to analyze by the mean-field theory. Then the finite order parameters for various phases are rather to be regarded as properties of a corresponding Anderson-type model. In formally exact treatment of eq.(1), all of our order parameters would vanish identically in contrast with the results of the mean-field theory. However by the same reason as explained above for the two-impurity models, we would rather accept the results of the mean-field theory as a physically possible consequence for more realistic models.

5.2 Comparison with the f^1 lattice system

It is instructive to take the limits $I \rightarrow 0$ and $\Xi \rightarrow 0$ in eq.(1). Then the system becomes equivalent to two independent Kondo lattices. In the half-filled case the ground state is either the Kondo insulator or a magnetically ordered phase. The latter state is due to the RKKY interaction which is not taken into account by the mean-field theory. We note that the ordered state can be either metallic or insulating depending on the magnetic structure. If it is ferromagnetic, the half-filled conduction band leads to the metallic state. As one increases J from zero, the ground state should change from the magnetically ordered state to the insulating one. Subsequently the nature of f electrons changes from the localized character to the itinerant one. Since the entropy is different in the two phases, a phase transition can occur from one phase to the other as a function of temperature.

Let us compare this phase transition with another one which is known as an artifact of the mean-field theory. Namely, as temperature increases in the mean-field theory, the order parameter Δ of the Kondo insulating phase decreases continuously to zero around the temperature $T \sim T_K$. In the exact theory the local gauge fluctuation washes away the transition completely. We emphasize that the possible transition between the Kondo insulator and the magnetically ordered phase should survive the fluctuation effect.

Now we consider the case of finite I and Ξ . In the mean-field theory, the Kondo insulating phase does not feel the effect of I and Ξ . The resultant state is the same as the direct product of the two f^1 lattices. Hence the second-order transition around $T \sim T_K$ is again fictitious. One can ask at two temperature how the magnetic state changes as I increases continuously from 0. For small I , we have the ordered induced moment which arises by mixing of the singlet and triplet levels. At certain critical value of I , the CEF singlet will become more stable than the induced moment. The situation is analogous to the spin chain problem where exchange interactions of alternating strength form dimers with an excitation gap. We note that the f electrons are always localized for any value of I . Thus the change to the Kondo insulator can occur as a phase transition, although both states are spin singlets.

5.3 Effects of charge fluctuation on the phase transition

In actual f^2 lattice systems there should always be charge fluctuation as discussed above. Then any exact eigenstate has some amount of hybridization between f and conduction electrons. However, there can still be two different kinds of hybridized states: The first one can be reached by perturbation theory with respect to hybridization. This state is connected with the localized f^2 state. The other state is the itinerant state which is not accessible by such perturbation theory. The latter state instead is simply described by the band picture of f electrons. Thus possibility of the phase transition remains even though effects of charge fluctuations are included.

We note that the transition to the CEF singlet phase is of first order. A first-order transition should be less sensitive to fluctuation effects than a second-order one. We plan to check the robustness of the phase transition by using theories [5, 6, 7] more reliable than the mean-field theory.

5.4 Possible experimental relevance

With respect to experimental relevance, we have to consider also the case where the number of conduction electrons deviates from $2N_s$. In the Anderson lattice model with dominant f^2 configurations, the itinerant state then has a finite density of states of f electrons at the Fermi level, and hence is metallic. In this case the Fermi level is shifted from the center of the hybridization gap, and the average occupation of f electrons per site also deviates from 2. Thus in reality the transition from the itinerant state to the localized one is not always an insulator-metal transition.

Concerning possible relevance of our theory, we mention two uranium compounds: UNiSn and URu₂Si₂. In the former case, the insulating state at high temperatures changes via a first-order transition into a metallic state at $T = 43$ K. In contrast to our model, however, the metallic state shows the antiferromagnetic order [8]. As long as the localized picture applies to the low-temperature phase, the driving force of the transition may be similar to the one discussed in this paper. It is necessary to include the induced moment for more detailed analysis of UNiSn. In the latter case of URu₂Si₂, the CEF singlet model accounts for gross features of highly anisotropic susceptibility and metamagnetic transition [9]. The high-temperature phase is metallic showing the Kondo effect in the resistivity. A clear anomaly

in the specific heat is observed at temperature $T_0 = 17.5$ K [10], and the resistivity shows the metallic behavior also below T_0 . By neutron scattering [11] the antiferromagnetically ordered magnetic moments were observed below T_0 . The magnitude of the moment is only $0.04\mu_B$ which is smaller by two orders of magnitude than the usual magnitude observed in similar compounds UT_2Si_2 ($T = Pd, Rh$). Moreover, the growth of moments with decreasing temperature does not follow the mean-field behavior. Strangely, the NMR does not probe the internal field below T_0 [12]. Thus there is a possibility that the apparent antiferromagnetism is not a true long-range order, but due to very slow fluctuation of U moments.

In any case the specific heat jump at T_0 is too large to be accounted for by the tiny magnetic moment. Thus, the proper order parameter in this ordered phase remains to be identified [13, 14, 15, 16]. We note that the inelastic neutron scattering [11] probed a feature which looks like a CEF excitation below T_0 . This fact may be a key to identify the order parameter. The phase transition seems to be of second order.

In summary, we have shown that the phase transition from the itinerant state to the CEF singlet state occurs as temperature decreases in the f^2 lattice system in the frame of the mean-field theory. Properties of the f^2 lattice system were discussed in comparison with the two-impurity system at zero and finite temperatures. We suggest that the competition between localized and itinerant states of f electrons is the fundamental driving force for phase transitions in some uranium compounds such as $UNiSn$ and URu_2Si_2 . It remains to see to what extent the fluctuation effect beyond the mean-field theory affects the phase transition.

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Figure 1: The ground-state energies of (a) the f^2 lattice system, and (b) the two-impurity system. In (a), E_K , E_{CEF} and E_{mix} correspond to the Kondo (itinerant), CEF (localized) and mixed states, respectively, and Ξ is a parameter to characterize the strength of intersite hybridization. In (b), E_K , E_{ffpair} and E_{mix} show the energies of Kondo-pair, pair-singlet and mixed states, respectively. The parameter B ($|B| \leq 1$) characterizes the strength of intersite hybridization effect. Another hybridization parameter A is fixed to be -0.2 (see text).

Figure 2: Free energies of (a) the f^2 lattice system and (b) the two-impurity system. In (a), F_K , F_{CEF} and F_{mix} indicate the Kondo (itinerant), CEF and mixed states, respectively. In (b), F_K , F_{ffpair} and F_{mix} indicate the Kondo-pair, pair-singlet and mixed states, respectively. The parameter A is fixed to be -0.2 as in Fig.1.

Table 1: Parameters for calculation.

D	T_K	I	Ξ
10^4 [K]	1 [K]	$0 \sim 10$ [K]	-1 \sim 1



